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In re the Application of:

Ho-Jin Kweon, et al.

Application No. 10/627,725

Group Art Unit: 1795

Confirmation No. 7093

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For: POSITIVE ACTIVE MATERIAL FOR RECHARGEABLE LITHIUM BATTERY AND
METHOD OF PREPARING SAME

SUBMISSION OF VERIFIED TRANSLATION OF PRIORITY DOCUMENT

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

Applicants submit herewith translations of Korean Patent Application No. 2000-59336 claiming priority to October 9, 2000 and Korean Patent Application No. 2001-26468 claiming priority to May 15, 2001 and a statement from the translator.

If there are any fees associated with filing of this Submission, please charge the same to our Deposit Account No. 503333.

Respectfully submitted,

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Verification Statement For Translation

I, KIM, Hyo-Jin, hereby declare that I am conversant in the Korean and the English languages and that I am the translator of the document attached and certify that to the best of my knowledge and belief the following are true and correct English translations of the specification contained in Korean Patent Application Nos. 2001-0026468 and 2000-0059336.

Signature :

Hyo-Jin Kim

KIM, Hyo-Jin

Date :

March 30, 2009

ABSTRACT OF THE DISCLOSURE

[Abstract]

The present invention relates a positive active material for a rechargeable lithium battery and a method of preparing the same, and the positive active material includes a core including at least one lithiated compound represented by the formulas 1 to 14,

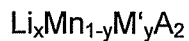
(formula 1)



(formula 2)



(formula 3)



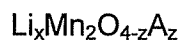
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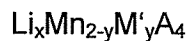
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(formula 6)



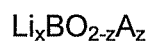
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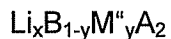
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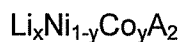
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(formula 10)



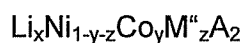
(formula 11)



(formula 12)



(formula 13)



(formula 14)



where

$$0.95 \leq x \leq 1.1, 0.01 \leq y \leq 0, 0.01 \leq z \leq 0.5, 0.95 \leq x' \leq 1, 0.01$$

$$\leq y' \leq 0.5, 0 \leq z' \leq 0.1, 0.01 \leq \alpha \leq 0.5,$$

M' is at least one lanthanoid or transition metal selected from the group consisting of Al, Cr, Mn, Fe, Mg, La, Ce, Sr and V,

M'' is at least one lanthanoid or transition metal selected from the group consisting of Al, Cr, Co, Mg, La, Ce, Sr and V,

A is selected from the group consisting of O, F, S and P, and

B is selected from the group consisting of Ni or Co.

[REPRESENTATIVE DRAWING]

Fig. 1

[Key words]

metal hydroxide, positive active material, rechargeable lithium battery

[SPECIFICATION]

[TITLE OF THE INVENTION]

POSITIVE ACTIVE MATERIAL FOR RECHARGEABLE LITHIUM
BATTERY AND METHOD OF PREPARING SAME

[BRIEF DESCRIPTION OF THE DRAWINGS]

FIG. 1 is a schematic diagram showing an apparatus used in a coating step of the present invention;

FIG. 2 is a schematic diagram illustrating a production process of a positive active material with LiCoO_2 according to the present invention;

FIG. 3 is a schematic diagram illustrating a production process of a positive active material with LiCoO_2 according to the conventional procedure;

FIG. 4 is a block diagram illustrating an inventive procedure with a one-shot process and the conventional procedure.

FIG. 5a is a scanning electronic microscope (SEM) view showing a surface of a positive active material according to one embodiment of the present invention;

FIG. 5b is a SEM view showing a surface of a positive active material according to another embodiment of the present invention;

FIG. 5c is a SEM view showing a surface of a positive active material according to Comparative example 5;

FIG. 5d is a SEM view showing a surface of a LiCoO_2 positive active material;

FIG. 6 is a graph illustrating the discharge characteristics at 0.1C of positive active materials according to Examples of the present invention and

Comparative examples;

FIG. 7 is a graph illustrating the discharge characteristics at 0.5C of positive active materials according to Examples of the present invention and Comparative example;

FIG. 8 is a graph illustrating the discharge characteristics at 1C of positive active materials according to Examples of the present invention and Comparative examples;

FIG. 9 is a graph illustrating the XRD pattern of $\text{Al}(\text{OH})_3$ and Al_2O_3 ; and

FIG. 10 is JCPDS cards of $\text{Al}(\text{OH})_3$ and Al_2O_3 .

[DETAILED DESCRIPTION OF THE INVENTION]

[OBJECT OF THE INVENTION]

[DESCRIPTION OF THE RELATED ART]

[Field of the Invention]

The present invention relates to a positive active material for a rechargeable lithium battery and a method of preparing the same, and, more particularly, to a positive active material for a rechargeable lithium battery exhibiting good electrochemical properties such as cycle life, high discharge potential, high power density and improved thermal stability characteristics.

[Description of the Related Art]

Rechargeable lithium batteries have high average discharge potential of about 3.7V and are 4V-grade batteries, and the rechargeable lithium batteries are widely used for cellular phones, notebook computers, or camcorders, which are also known as "the 3Cs", and are main components in the digital world. For the positive active material in the rechargeable lithium

battery, most rechargeable lithium batteries, about at least 95% employ LiCoO_2 . Although LiCoO_2 exhibits good cycle life characteristics and good flat discharge profiles, there are still demands to improve electrochemical properties such as good cycle life and high power density.

One way to satisfy such a demand is to substitute a part of the Co from LiCoO_2 with other metals. Sony prepares $\text{Li}_x\text{Co}_{1-y}\text{M}_y\text{O}_2$ by doping about 1 to 5 percent by weight of Al_2O_3 into LiCoO_2 . A&TB (Ashai & Thosiba Battery Co.) prepares a Sn-doped Co-based active material by substituting a part of Co from LiCoO_2 with Sn. Another way is that a lithiated compound is coated with a coating material. Korean Patent Application No. 98-3755, which is assigned to the assignee of the present invention discloses that a treated LiCoO_2 is prepared by coating LiCoO_2 with a metal-alkoxide solution and heat-treating. Even though these studies have progressed, there are still demands for improving electrochemical properties such as high capacity, long cycle life, high power density and exhibiting good thermal stability.

[SUBJECT MATTER OF THE INVENTION]

It is an object of the present invention to provide a positive active material for a rechargeable lithium battery exhibiting good electrochemical properties such as good cycle life, high discharge potential and high power density.

It is another object to provide a method of preparing the same.

[ELEMENTS AND WORKING EXAMPLES OF THE INVENTION]

These and other objects may be achieved by a positive active material

for a rechargeable lithium battery including a core including at least one lithiated compound represented by formulas 1 to 14; and an amorphous or crystalline metal hydroxide layer on the core.

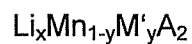
(formula 1)



(formula 2)



(formula 3)



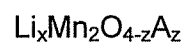
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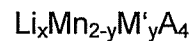
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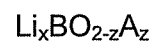
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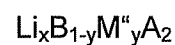
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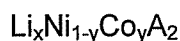
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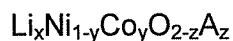
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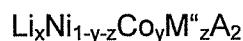
(formula 11)



(formula 12)



(formula 13)



(formula 14)



where

$$0.95 \leq x \leq 1.1, 0.01 \leq y \leq 0, 0.01 \leq z \leq 0.5, 0.95 \leq x' \leq 1, 0.01$$

$$\leq y' \leq 0.5, 0 \leq z' \leq 0.1, 0.01 \leq \alpha \leq 0.5,$$

M' is at least one lanthanoid or transition metal selected from the group consisting of Al, Cr, Mn, Fe, Mg, La, Ce, Sr and V,

M'' is at least one lanthanoid or transition metal selected from the group consisting of Al, Cr, Co, Mg, La, Ce, Sr and V,

A is selected from the group consisting of O, F, S and P, and

B is selected from the group consisting of Ni or Co.

In order to achieve these objects and others, the present invention provides a method of preparing a positive active material for a rechargeable lithium battery, including coating at least one lithiated compound represented by formulas 1 to 14 with a solution of metal alkoxide or an aqueous solution of metal, and drying the coated compound.

The present invention will be illustrated in more detail.

The present invention is an improvement of Korean Patent Application, which is assigned to the assignee of the present invention and which discloses mixing a solution of metal alkoxide with metal oxide powder (LiCoO_2 , $\text{LiNi}_{1-x-y}\text{M}_x\text{N}_y\text{O}_2$) to prepare a slurry and drying the slurry followed by the heat-treatment at about 300 to 800°C to prepare a positive active material coated with metal oxide layer. Whereas, a method of the present invention includes no heat-treatment and includes drying so that a positive active material coated with metal hydroxide layer rather than metal oxide layer is prepared.

A positive active material of the present invention includes a core including at least one lithiated compound represented by formulas 1 to 14 and a metal hydroxide layer formed on the core.

The metal in the metal hydroxide layer may be any element which is capable of dissolving in organic solvents or water, and examples are Mg, Al, Co, K, Na, Ca, Si, Ti, V, Ge, Ga, or B.

The positive active material of the present invention exhibits improved electrochemical properties in cycle life, discharge potential, power density and good thermal stability, compared with conventional LiCoO_2 or $\text{LiNi}_{1-x-y}\text{M}_x\text{N}_y\text{O}_2$ which is commercially available.

In order to prepare a positive active material of the present invention, at least one lithiated compound represented by formulas 1 to 14 is coated (encapsulated) with a solution of metal alkoxide or an aqueous solution of metal.

The coating process may be performed by a sputtering method, a CVD (chemical vapor deposition) method, a dip coating, or by using any other

general-purpose coating technique. A common method of the coating process is dipping the lithiated compound in the solution and the dipping methods include one where the lithiated material is mixed with the coating solution, and the resulting lithiated material is then separated from the solution.

Alternatively, the coating process may be a one-shot process where a mixing step, a solvent-removing step and a drying step take place in a single process vessel, and this one-shot process is simple, thereby reducing the production cost and making a uniform surface-treatment layer on a core. The one-shot process may be performed such that at least one compound represented by formulas 1 to 14 (lithiated compound) and the coating solution is injected into a mixer and the temperature of the mixer is raised while shaking the mixer followed by injection of inert gas such as nitrogen gas or argon gas into the mixer. While the coating solution is coated on the lithiated compound, excess coating solution may be evaporated and removed by increasing the ambient temperature and mixing. Thus, the mixing step, the solvent removing step, and the drying step are performed in a single mixer vessel. In order for a more uniform mix, the mixture may be premixed for about 10 to 30 min prior to the mixing step.

The increase in the temperature of the mixer may be achieved by circulating hot water having a temperature at which the organic solvent or water is evaporated, preferably about 50 to 100°C around the mixer, the hot water may be cooled by circulating it around the mixer, and the cooled water may be heated by a heat exchanger, at which time and the heated water may then be

re-circulated.

The mixer may be any mixer so long as the lithiated compound and the coating solution are well mixed and the temperature of the mixer is raised during the mixing process. Preferred is a mixer into which the blowing gas can be injected and which can keep a vacuum condition. Exemplary of the mixer may be a planetary mixer. FIG. 1 presents a mixer with a heat exchanger. As shown in FIG. 1, an inert gas such as nitrogen gas is injected into the upper portion of the mixer while the hot water is circulated through the heat exchanger around the mixer.

The solution of metal alkoxide is obtained by mixing an alcohol with metal of 0.1 to 10 % by weight of the alcohol, and preferably refluxing the resulting mixture. Alternatively, the solution with a concentration of 0.1 to 10 wt% is prepared by dissolving metal alkoxide in an alcohol. The aqueous solution of metal is prepared by mixing water with metal or metal oxide of 0.1 to 10 % by weight of water, and preferably refluxing the resulting mixture. The coating element in the coating material source may be any element which is capable of dissolving in organic solvents or water. Examples are Mg, Al, Co, K, Na, Ca, Si, Ti, V, Ge, Ga, or B or any mixture thereof. The metal alkoxide may be metal methoxide, metal ethoxide or metal propoxide, and the alcohol may be methanol, ethanol or isopropanol. The aqueous solution of metal may be an aqueous solution of vanadium oxide (V_2O_5).

When the concentration of the metal is below 0.1 percent by weight, the effect obtained by coating the solution onto the lithiated compound represented by formulas 1 to 14 may not be sufficient. In contrast, when the concentration

of coating material source is more than 10 percent by weight, the resultant coating layer may become undesirably thick.

Thereafter, the coated powder may be dried from room temperature to about 200°C for approximately 1 to 24 hours.

As a result, the solution of metal alkoxide or the aqueous solution of metal reacts with moisture in atmosphere so that it is converted into metal-oxy hydroxide and then finally metal hydroxide. The forming procedure of the metal hydroxide layer is schematically illustrated in FIG. 2. The metal hydroxide layer reduces the internal resistance and prevents the discharge potential drop so that the active material exhibits high discharge potential, and as a result, the positive active material of the present invention provides good cycle life characteristics, discharge potential, and power.

As described above, this inventive procedure includes the mixing step and the drying step. The conventional procedure includes the mixing step, the drying step, and the heat-treating step (FIG. 3). When the heat-treating step is performed, a metal oxide layer is formed on the core. The metal oxide layer has relatively low ionic conductivity, which causes the internal resistance to increase and the discharge potential and power density to deteriorate. On the other hand, when the heat-treating step is not performed, a metal hydroxide layer is formed on the core, and the resulting positive active material exhibits superior charge and discharge characteristics as compared to that of metal oxide-coated positive active material.

For reference purposes, the one-shot process is compared with the

conventional process below, and their procedures are illustrated in FIG. 4. As shown in FIG. 4, the conventional coating process is such that the coating element-containing organic solution or aqueous solution is mixed with the lithiated compound to make a slurry (mixing step). The resulting lithiated compound is separated from the solution (solvent removing step), the separated lithiated compound is dried, perhaps at 80 to 100°C (drying step), and then the dried compound is heat-treated.

The inventive procedure, also shown in FIG. 4, includes a one-shot process (including the mixing step, the solvent removing step and the drying step in a single vessel) so that the total procedure is simple and economical. Furthermore, this procedure uniformly coats the lithiated compound with the metallic alkoxide solution or aqueous solution of metal. In addition, the inventive procedure can form a metal hydroxide layer on the core rather than the metal oxide layer.

The lithiated compound represented by formulas 1 to 14 may be available commercially or may be produced by the following procedure.

In order to synthesize the lithiated compound represented by formulas 1 to 14, lithium sources are mixed with metal sources in a desirable ratio. The lithium source may be any material known in the related art, some of which include lithium nitrate, lithium acetate, and lithium hydroxide. For the metal sources, manganese sources, cobalt salts, nickel sources, or nickel-manganese sources may be used. Typical examples of the manganese sources are manganese acetate and manganese dioxide. Typical examples

of the cobalt sources are cobalt hydroxide, cobalt nitrate and cobalt carbonate, whereas typical examples of the nickel sources are nickel hydroxide, nickel nitrate, and nickel acetate. The nickel-manganese sources are produced by co-precipitating nickel and manganese salts. Fluoride sources, sulfur sources or phosphorous sources may be further used together with the manganese sources, cobalt sources, nickel sources or nickel-cobalt sources. The fluoride sources may be manganese fluoride or lithium fluoride and the sulfur sources may be manganese sulfide or lithium sulfide. The phosphorous sources may be H_3PO_4 . Note that the above list of manganese, cobalt, nickel, nickel-manganese, fluoride, sulfur and phosphorus sources is not an exclusive list.

The mixing procedure may be performed by mortar grinder mixing, and at this time, in order to facilitate the reaction of the lithium sources and the metal sources, a solvent such as ethanol, methanol, water or acetone is added to the mixture, and the mixture is then mortar grinder mixed until a liquid-free condition is reached.

The resulting mixture is heat-treated at about 400 to 600°C to produce a semi-crystalline positive active material precursor powder. Although other temperatures are possible, if the first heat-treating step temperature is less than 400°C, the metal sources may not react completely with the lithium sources. Thereafter, the heat-treated active material precursor powder is dried under dry air or oxygen, and the precursor powder is remixed to uniformly distribute the lithium sources. Alternatively, the remixing step may be performed immediately after the heat-treating step.

The semi-crystalline precursor powder is again heat-treated at about 700 to 900°C for about 10 to 15 hours to produce a crystalline positive active material. If the second heat-treating step temperature is less than 700°C, it may be difficult to form a crystalline material. The heating step may be performed by increasing the temperature at a rate of 1 to 5°C/min under dry air. The mixture is allowed to stand at the first and second heat-treating temperature for predetermined amounts of time, and then mixture is naturally cooled.

As a result, a powder of a compound selected from the group consisting of the compounds represented by formulas 1 to 14 is obtained and thereafter, the compounds represented by formulas 1 to 14 are shaken at room temperature to uniformly distribute the lithium sources.

The following examples further illustrate the present invention.

Comparative example 1

A LiCoO_2 (Nippon Chem Co., Trademark: C-10) positive active material, a conductive agent and a binder at a weight ratio of 94 : 3 : 3 were mixed in N-methyl pyrrolidone to make a positive active material slurry. As the conductive agent, Super P was used, as the binder, polyvinylidene fluoride was used. The positive active material slurry is cast on an Al-foil with a thickness of about 100 μm to make a positive electrode. The positive electrode was punched at a diameter of 1.6cm, a coin-type half-cell was fabricated in a glove-box using the punched positive electrode, a 1M LiPF_6 in ethylene carbonate and dimethyl

carbonate electrolyte and a lithium metal foil counter electrode.

Comparative example 2

A coin-type half-cell was fabricated by the same procedure as in Comparative example 1, except that LiCoO_2 (UMEX Co.) was used.

Comparative example 3

A coin-cell was fabricated by the same procedure as in Comparative example 1, except that $\text{LiNi}_{0.9}\text{Sr}_{0.002}\text{Co}_{0.1}\text{O}_2$ positive active material (Honjo Co.) was used.

Comparative example 4

Five percent by weight of Al-isopropoxide was dissolved in 95 percent by weight of ethanol to prepare a 5% Al-isopropoxide ethanol solution. To the ethanol solution, LiCoO_2 (Nippon Chem Co., Trademark: C-10) was added, and then they were well mixed to sufficiently react the ethanol solution with LiCoO_2 followed by separating the resulting material from the solution and drying it at 100°C for about 12 hours in an oven. The dried material was heat-treated at about 500°C for approximately 10 hours under dry air to prepare a positive active material with an Al_2O_3 surface layer.

The positive active material, a Super P conductive agent and a polyvinylidene fluoride binder were mixed in N-methyl pyrrolidone in the weight ratio of 94 : 3 : 3 to make a positive active material slurry. The positive active material slurry is cast on an Al-foil with a thickness of about $100\ \mu\text{m}$ to make a positive electrode. The positive electrode was punched at a diameter of 1.6cm,

a coin-type half-cell was fabricated in a globe-box using the punched positive electrode, a 1M LiPF_6 in ethylene carbonate and dimethyl carbonate and a lithium metal foil counter electrode.

Comparative example 5

A coin-type half-cell was fabricated by the same procedure in Comparative example 4, except that 1% Al-isopropoxide ethanol solution was used and the heat-treatment was performed at 600°C.

Comparative example 6

A coin-type half-cell was fabricated by the same procedure in Comparative example 4, except that $\text{LiNi}_{0.9}\text{Sr}_{0.002}\text{Co}_{0.1}\text{O}_2$ positive active material (Honjo Co.) was used.

Comparative example 7

A coin-type half-cell was fabricated by the same procedure in Comparative example 6, except that 1% Al-isopropoxide ethanol solution was used.

Example 1

One percent by weight of Al-isopropoxide powder was dissolved in 99 percent by weight of ethanol to prepare a 1% Al-isopropoxide solution.

The Al-isopropoxide solution and LiCoO_2 (Nippon Chem Co., Trademark: C-10) were injected into a mixer shown in FIG. 1 and they were mixed for about 10 minutes. The temperature of an incubator was set to about 60°C, and the mixing step was performed for about 1 hour while the water was circulating and N_2 gas was purging to prepare a LiCoO_2 positive active material

powder with $\text{Al}(\text{OH})_3$ surface layer.

The positive active material powder, a conductive agent, and a binder were mixed in a N-methyl pyrrolidone solvent at a ratio of 94 : 3 : 3 to make a positive active material slurry. As the conductive agent, Super P was used, and as the binder, polyvinylidene fluoride was used. The positive active material slurry was cast on an Al-foil with a thickness of about 100 μm to make a positive electrode. The positive electrode was punched with a diameter of 1.6cm, and a coin-type half-cell was fabricated in a glove-box using the positive electrode, a 1M LiPF_6 in ethylene carbonate and dimethyl carbonate electrolyte, and a lithium metal counter electrode.

Example 2

A coin-type half-cell was fabricated by the same procedure in Comparative Example 4, except that a heat-treatment was not performed after drying.

Example 3

A coin-type half-cell was fabricated by the same procedure in Comparative Example 5, except that a heat-treatment was not performed after drying.

Example 4

A coin-type half-cell was fabricated by the same procedure in Comparative Example 6, except that a heat-treatment was not performed after drying.

Example 5

A coin-type half-cell was fabricated by the same procedure in Example 2, except that a $\text{LiNi}_{0.9}\text{Sr}_{0.002}\text{Co}_{0.1}\text{O}_2$ positive active material (Honjo Co.) was used.

Example 6

A coin-type half-cell was fabricated by the same procedure in Example 2, except that a 5% Al-isopropoxide solution was used.

The SEM photographs of the positive active materials according to Examples 2 and 3, and Comparative example 4 are presented in FIGs. 5a, 5b and 5c, respectively. For comparison, SEM photograph of pure LiCoO_2 is presented in FIG. 5d. As shown in FIGs. 5a-d, the positive active materials according to Examples 2 and 3 (FIGs. 5a and 5b) have similar smooth surface to that of LiCoO_2 (FIG. 5d), but the positive active material according to Comparative example 5 (FIG. 5c) has an uneven surface due to the metal oxide mass.

The positive active materials according to Examples 2 to 3, Comparative Example 1, and LiCoO_2 (Nippon Chme Co., Trademark: C-10), were charged and discharged at 0.1C, 0.5C and 1C, respectively, and the discharge characteristics thereof are shown in FIGs. 6 to 8, respectively. As shown in FIGs. 6 to 8, the positive active materials according to Examples 2 to 5 exhibited slightly better discharge characteristics than those of Comparative example 1 at a low rate (FIG. 6, 0.1C), but at high rate (FIG. 7, 0.5C; FIG. 8, 1C) Examples 2 to 5 exhibited surprisingly better discharge characteristics than that of Comparative example 1.

The positive active material according to Comparative example 1 had a

surface layer including metal oxide with relatively low ionic conductivity which causes increase in the internal resistance and reduced discharge potential and power, and on the other hand, the metal hydroxide layer in the positive active materials according to Examples 2 to 3 had relatively low internal resistance so that it exhibits low discharge potential drop and high discharge potential retention. Thus, it is expected that the cell with the positive active material of Example 2 to 3 exhibited good cycle life characteristics, discharge potential characteristics and improved power density.

In order to identify amorphous $\text{Al}(\text{OH})_3$ and Al_2O_3 , the XRD pattern thereof were measured. The amorphous $\text{Al}(\text{OH})_3$ and Al_2O_3 were prepared by mixing 5g of a Al-isopropoxide solution and 95g of ethanol and mixing them for about 3 hours to obtain clear Al-isopropoxide solution followed by dividing the solution into three beakers, drying the No. 1 beaker at about room temperature for about 1 day, and the No. 2 beaker in an approximately 130°C oven for about 1 day, and heat-treating the No. 3 beaker in an approximately 600°C furnace for about 1 day. The XRD pattern of the amorphous $\text{Al}(\text{OH})_3$ and Al_2O_3 are shown in FIG. 9. It is evident from FIG. 9 that the XRD pattern of amorphous $\text{Al}(\text{OH})_3$ is distinct from that of amorphous Al_2O_3 .

In addition, as shown in FIG. 9, both powder (drying at 130°C, and heat-treating at 600°C) had amorphous patterns. It is considered that the powder dried at 130°C is $\text{Al}(\text{OH})_3$ presented in JCPDS No. 83-2256 and that heat-

treated at 600°C is amorphous Al_2O_3 presented in JCPDS No. 02-1373, when they are compared with the reference datum in JCPDS cards of FIG. 10. Accordingly, it is expected that the positive active materials according to Examples have amorphous coating layer.

[Effect of the invention]

In summary, the positive active material of the present invention has metal hydroxide layer having good ionic conductivity, which reduces internal resistance and prevents the discharge potential drop. The positive active material of the present invention provides rechargeable lithium battery exhibiting good cycle life characteristics, high discharge potential and high power.

[WHAT IS CLAIMED IS:]

1. A positive active material for a rechargeable lithium battery comprising

a core comprising at least one lithiated compound represented by formulas 1 to 14; and

an amorphous or crystalline metal hydroxide layer on the core.

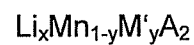
(formula 1)



(formula 2)



(formula 3)



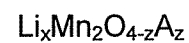
(formula 4)



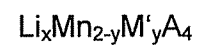
(formula 5)



(formula 6)



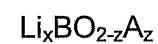
(formula 7)



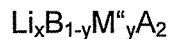
(formula 8)



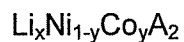
(formula 9)



(formula 10)



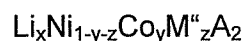
(formula 11)



(formula 12)



(formula 13)



(formula 14)



where

$$0.95 \leq x \leq 1.1, 0.01 \leq y \leq 0, 0.01 \leq z \leq 0.5, 0.95 \leq x' \leq 1, 0.01$$

$$\leq y' \leq 0.5, 0 \leq z' \leq 0.1, 0.01 \leq \alpha \leq 0.5,$$

M' is at least one lanthanoid or transition metal selected from the group consisting of Al, Cr, Mn, Fe, Mg, La, Ce, Sr and V,

M'' is at least one lanthanoid or transition metal selected from the group consisting of Al, Cr, Co, Mg, La, Ce, Sr and V,

A is selected from the group consisting of O, F, S and P, and

B is selected from the group consisting of Ni or Co.

2. The positive active material of claim 1 wherein the metal is soluble in alcohol or water.

3. A method of preparing a positive active material for a

rechargeable lithium battery comprising:

coating at least one lithiated compound represented by formulas 1 to 14 with a solution of metal alkoxide or an aqueous solution of metal to produce a coated compound; and

drying the coated compound.

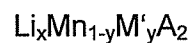
(formula 1)



(formula 2)



(formula 3)



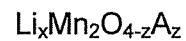
(formula 4)



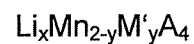
(formula 5)



(formula 6)



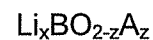
(formula 7)



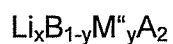
(formula 8)



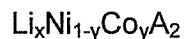
(formula 9)



(formula 10)



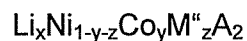
(formula 11)



(formula 12)



(formula 13)



(formula 14)



where

$$0.95 \leq x \leq 1.1, 0.01 \leq y \leq 0, 0.01 \leq z \leq 0.5, 0.95 \leq x' \leq 1, 0.01$$

$$\leq y' \leq 0.5, 0 \leq z' \leq 0.1, 0.01 \leq \alpha \leq 0.5,$$

M' is at least one lanthanoid or transition metal selected from the group consisting of Al, Cr, Mn, Fe, Mg, La, Ce, Sr and V,

M'' is at least one lanthanoid or transition metal selected from the group consisting of Al, Cr, Co, Mg, La, Ce, Sr and V,

A is selected from the group consisting of O, F, S and P, and

B is selected from the group consisting of Ni or Co.

4. The method of claim 3 wherein the coating step is performed by injecting the lithiated compound and the solution of metal alkoxide or the aqueous solution of metal into a mixer and continuously increasing the temperature within the mixer while injecting an inert gas into the mixer.

ABSTRACT OF THE DISCLOSURE

[Abstract]

The present invention relates to a positive active material for a rechargeable lithium battery and a method of preparing the same, and the positive active material includes a core including at least one lithiated compound and the surface-treatment layer on the core, and the surface-treatment layer including at least one coating material selected from the group consisting of coating element included-hydroxides, oxyhydroxides, oxycarbonates, hydroxycarbonates and any mixture thereof.

[REPRESENTATIVE DRAWING]

Fig. 11

[Key words]

metal hydroxide, surface-treatment, positive active material, rechargeable lithium battery, thermal stability

[SPECIFICATION]

[TITLE OF THE INVENTION]

POSITIVE ACTIVE MATERIAL FOR RECHARGEABLE LITHIUM
BATTERY AND METHOD OF PREPARING SAME

[BRIEF DESCRIPTION OF THE DRAWINGS]

FIG. 1 is a schematic diagram showing an apparatus used in a coating step of the present invention;

FIG. 2 is a schematic diagram illustrating a production process of a positive active material with LiCoO_2 according to the present invention;

FIG. 3 is a schematic diagram illustrating a production process of a positive active material with LiCoO_2 according to the conventional procedure;

FIG. 4 is a block diagram illustrating an inventive procedure with a one-shot process and the conventional procedure.

FIGs. 5a to 5d are a scanning electronic microscope (SEM) views showing a surface of a positive active material according to Examples of the present invention and Comparative Example;

FIGs. 6a and 6b are a transmission electronic microscopy (TEM) views of a positive active material for a rechargeable lithium battery according to Example of the present invention and Comparative Example;

FIG. 7 is a graph illustrating the X-ray diffraction (XRD) pattern of positive active materials according to Examples and Comparative example of the present invention;

FIG. 8 is a graph illustrating the discharge characteristics at 0.1C of

positive active materials according to Examples and Comparative examples of the present invention;

FIG. 9 is a graph illustrating the discharge characteristics at 1C of positive active materials according to Examples and Comparative examples of the present invention;

FIG. 10 is a graph illustrating the cycle life characteristics of positive active materials according to Examples and Comparative example of the present invention;

FIG. 11 is a graph illustrating the cycle life characteristics at high temperature of positive active materials according to Examples and Comparative example of the present invention;

FIG. 12 is a graph illustrating the differential scanning calorimetry (DSC) results of positive active materials of Examples and Comparative examples according to the present invention;

FIG. 13 is a graph illustrating the DSC results of positive active materials of Example and Comparative example of the present invention;

FIGs. 14a and 14b is a picture of a cylindrical cell prior to and after a thermal stability test according to Comparative example and Example of the present invention;

FIG. 15 is a FT-IR graph of a coating material of a positive active material of the present invention;

FIG. 16 is a Raman spectrum of a surface-treatment layer of a positive active material of the present invention and Al_2O_3 ;

FIG. 17 is a graph illustrating the XRD pattern of $\text{Al}(\text{OH})_3$ and Al_2O_3 ;

FIG. 18 is JCPDS cards of $\text{Al}(\text{OH})_3$ and Al_2O_3 ; and

FIG. 19 is a graph illustrating the XRD pattern of coating material of a positive active material of the present invention and B_2O_3 .

[DETAILED DESCRIPTION OF THE INVENTION]

[OBJECT OF THE INVENTION]

[DESCRIPTION OF THE RELATED ART]

[Field of the Invention]

The present invention relates to a positive active material for a rechargeable lithium battery and a method of preparing the same, and, more particularly, to a positive active material for a rechargeable lithium battery exhibiting good electrochemical properties such as cycle life, high discharge potential, high power density and improved thermal stability characteristics.

[Description of the Related Art]

Rechargeable lithium batteries have high average discharge potential of about 3.7V and are 4V-grade batteries, and the rechargeable lithium batteries are widely used for cellular phones, notebook computers, or camcorders, which are also known as "the 3Cs", and are main components in the digital world.

The rechargeable lithium batteries use a material from or into which lithium ions are deintercalated or intercalated as positive and negative active materials. For an electrolyte, an organic solvent or polymer is used. Rechargeable lithium batteries produce electric energy as a result of changes in the chemical potentials of the active materials during the intercalation and deintercalation reactions of lithium ions.

For the negative active material in a rechargeable lithium battery, metallic lithium has been used in the early days of development, and recently, however, carbon materials, which intercalate lithium ions reversibly, are extensively used instead of the metallic lithium due to problems of high reactivity toward electrolyte and dendrite formation of the metallic lithium. In particular, boron is added to carbonaceous materials to produce boron-coated graphite (BOC) in order to increase the capacity of the carbonaceous materials.

For the positive active material in the rechargeable lithium battery, chalcogenide compounds into or from which lithium ions are intercalated or deintercalated are used, and typical examples include LiCoO_2 , LiMn_2O_4 , LiNiO_2 , $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$ ($0 < x < 1$) or LiMnO_2 . Manganese-based materials such as LiMn_2O_4 or LiMnO_2 are the easiest to prepare, are less expensive than the other materials, and are environmentally friendly, but manganese-based materials have a low capacity. LiNiO_2 is inexpensive and has a high charge capacity, but is difficult to produce. LiCoO_2 is relatively expensive, but widely used by Sony as it has good electrical conductivity and high battery voltage. Most rechargeable lithium batteries, about at least 95%, employ LiCoO_2 . Although LiCoO_2 exhibits good cycle life characteristics and good flat discharge profiles, there are still demands to improve electrochemical properties such as good cycle life and high power density.

One way to satisfy such a demand is to substitute a part of the Co from LiCoO_2 with other metals, and this way includes that Sony prepares $\text{Li}_x\text{Co}_{1-y}\text{M}_y\text{O}_2$ by doping about 1 to 5 percent by weight of Al_2O_3 into LiCoO_2 , and A&TB (Ashai & Thosiba Battery Co.) prepares a Sn-doped Co-based active material

by substituting a part of Co from LiCoO_2 with Sn.

U.S. Patent No. 5,292,601 discloses Li_xMO_2 (M is at least one element selected from Co, Ni or Mn; x is 0.5 to 1). U.S. Patent No. 5,705,291 discloses a method in which a coating material selected from boron oxide, boric acid, lithium hydroxide, aluminum oxide, lithium aluminate, lithium metaborate, silicon dioxide, lithium silicate or mixtures thereof, is mixed with a lithiated intercalation compound, and the mixture is annealed at 400°C or more to coat the compound with the coating material.

Japanese Patent Laid-Open No. Hei 9-55210 discloses that lithium nickel-based oxide is coated with alkoxide of Co, Al and Mn and heat-treated to prepare a positive active material, Japanese Patent Laid-Open No. Hei 11-16566 discloses lithium-based oxide coated with a metal such as includes Ti, Sn, Bi, Cu, Si, Ga, W, Zr, B or Mn, and/ or an oxide thereof, and Japanese Patent Laid-Open No. 11-185758 discloses coating a surface of lithium manganese oxide with metal oxide by using a co-precipitation procedure and heat-treating the same to prepare a positive active material.

Even though these studies have progressed, there are still demands for improving electrochemical properties such as high capacity, long cycle life, high power density and exhibiting good thermal stability. In addition, much research is being conducted on thermal stability of positive active materials to ensure stability and reliability of batteries under abusive condition such as heat-exposure, firing or overcharging.

[SUBJECT MATTER OF THE INVENTION]

It is an object of the present invention to provide a positive active material for a rechargeable lithium battery exhibiting good electrochemical properties such as good cycle life, high discharge potential and high power density.

It is another object to provide the positive active material for a rechargeable lithium battery with good thermal stability.

It is still another object to provide a method of preparing the same with an economical means.

[ELEMENTS AND WORKING EXAMPLES OF THE INVENTION]

These and other objects may be achieved by a positive active material for a rechargeable lithium battery including a core including at least one lithiated compound and a surface-treatment layer on the core, the surface-treatment layer including at least one coating material selected from the group consisting of coating element included-hydroxides, -oxyhydroxides, -oxycarbonates, -hydroxycarbonates and any mixture thereof..

In order to achieve these objects and others, the present invention provides a method of preparing a positive active material for a rechargeable lithium battery, including coating at least one lithiated compound with an organic solution of a coating material source or an aqueous solution of a coating material source, and drying the coated compound.

The present invention will be illustrated in more detail.

The present invention is an improvement of Korean Patent Application, which is assigned to the assignee of the present invention and which discloses

mixing a solution of metal alkoxide with metal oxide powder (LiCoO_2 , $\text{LiNi}_{1-x-y}\text{M}_x\text{N}_y\text{O}_2$) to prepare a slurry and drying the slurry followed by the heat-treatment at about 300 to 800°C to prepare a positive active material coated with metal oxide layer.

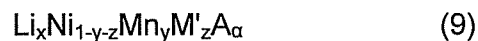
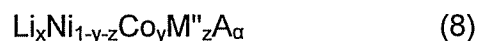
Whereas, a method of the present invention includes no heat-treatment and includes drying so that a positive active material coated with coating element included-hydroxides, -oxyhydroxides, -oxycarbonates, -hydroxycarbonates and any mixture thereof, layer rather than metal oxide layer is prepared.

A positive active material of the present invention includes a core including at least one lithiated compound and a surface-treatment layer on the core, the surface-treatment layer including at least one compound selected from the group consisting of coating element included-hydroxides, -oxyhydroxides, -oxycarbonates, -hydroxycarbonates and any mixture thereof.

The positive active material of the present invention exhibits improved electrochemical properties in cycle life, discharge potential, power density and good thermal stability, compared with conventional LiCoO_2 or $\text{LiNi}_{1-x-y}\text{M}_x\text{N}_y\text{O}_2$ which is commercially available.

The core includes at least one lithiated compound, and preferably includes at least one lithiated compound represented by the formulas 1 to 9,





where

$$0.95 \leq x \leq 1.1, 0 \leq y \leq 0.5, 0 \leq z \leq 0.5, 0 < \alpha \leq 2,$$

M is Ni or Co, M' is at least one element selected from the group consisting of Al, Ni, Co, Cr, Fe, Mg, Sr, V, Sc, Y, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Ac, Th, Pa, U, Np, Pu, Am, Cm, Bk, Cf, Es, Fm, Md, No and Lr, M'' is at least one element selected from the group consisting of Al, Cr, Mn, Fe, Mg, Sr, V, Sc, Y, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Ac, Th, Pa, U, Np, Pu, Am, Cm, Bk, Cf, Es, Fm, Md, No and Lr, and A is selected from the group consisting of O, F, S and P.

The surface-treatment layer includes at least one coating material selected from the group consisting of coating element included-hydroxides, -oxyhydroxides, -oxycarbonates, -hydroxycarbonates and any mixture thereof. The coating material may have amorphous or crystalline form. The coating element in the coating material may be any element which is capable of dissolving in organic solvents or water. Examples are Mg, Al, Co, K, Na, Ca, Si, Ti, V, Sn, Ge, Ga, B, As, Zr, or any mixture thereof.

A positive active material for a rechargeable lithium battery of the present invention is prepared by coating at least one lithiated compound with an organic solution or an aqueous solution of coating material source, and drying the coated compound.

In the present invention, the solution used in the coating step uses an organic solution or an aqueous solution of coating material source. The organic solution is obtained by dissolving a coating element or, a coating element included-alkoxide, -salt or -oxide in organic solvents, and preferably refluxing the resulting mixture. The aqueous solution is obtained by dissolving a coating element included-salt or -oxide in water, and preferably refluxing the resulting mixture. Suitable coating material source may be chosen from the coating element, the coating element included-alkoxide, -salt or -oxide according to the type of the solvent, which is well known to one skilled in the related arts. For example, if a boron-included coating solution is obtained by dissolving $\text{HB}(\text{OH})_2$, B_2O_3 , or H_3BO_3 in an organic solvent or water.

the organic solvents are used for the solvents, then the coating element, the coating element included-alkoxide, -salt or -oxide may be used for the coating material source, and if water is used for the solvents, then the coating element included-salt or -oxide may be used for the coating material source.

Useful organic solvents include hexane, chloroform, tetrahydrofuran, ether, methylene chloride, acetone, or alcohols such as methanol, ethanol or isopropanol.

An exemplary organic solution is a coating element-included alkoxide solution prepared by dissolving the coating element in an alcohol such as

methanol, ethanol or isopropanol, and refluxing them, or by dissolving a coating element-included alkoxide such as methoxide, ethoxide or isopropoxide in alcohol. For example, tetraethylorthosilicate solution is purchased from Aldrich Co. or is prepared by dissolving silicate in ethanol.

Useful salts or oxides include a form of vanadate, such as ammonium vanadate ($\text{NH}_4(\text{VO})_3$) or vanadium oxide (V_2O_5).

The concentration of coating material source in the coating solution may be 0.1 to 50 percent by weight based on the coating solution, and preferably 5 to 30 percent by weight. When the concentration thereof is below 0.1 percent by weight, the effect obtained by coating the solution onto the lithiated compound may not be sufficient. In contrast, when the concentration of coating material source is more than 50 percent by weight, the resultant coating layer may become undesirably thick.

At least one lithiated compound is coated (encapsulated) with the resulting organic solution or aqueous solution of the coating material source.

The coating process may be performed by a sputtering method, a chemical vapor deposition (CVD) method, a dip coating, or by using any other general-purpose coating technique. A common method of the coating process is dipping the lithiated compound in the solution and the dipping coating methods include one where the lithiated material is mixed with the coating solution, and the resulting lithiated material is then separated from the solution.

Alternatively, the coating process may be a one-shot process where a mixing step, a solvent-removing step and a drying step take place in a single process vessel. This one-shot process is simple, thereby reducing the

production cost and making a uniform surface-treatment layer including metal hydroxide, metal oxyhydroxide, metal oxycarbonate, metal hydroxycarbonate, or a mixture thereof, on a core.

The one-shot process may be performed such that at least one lithiated compound and the coating solution is injected into a mixer and the temperature of the mixer is raised while shaking the mixer. Additionally, blowing gas may be injected into the mixer and the blowing gas helps to facilitate evaporation of a solvent in the coating solution and to purge impure gases that are present in the mixer. The blowing gas may include CO₂ and moisture-free inert gas, such as nitrogen gas or argon gas. Alternatively, the one-shot process may be performed under a vacuum rather than using blowing gas.

While the coating solution is coated on the lithiated compound, excess coating solution may be evaporated and removed by increasing the ambient temperature and mixing. Thus, the mixing step, the solvent removing step, and the drying step are performed in a single mixer vessel. In order for a more uniform mix, the mixture may be premixed for about 10 to 30 min prior to the mixing step.

The increase in the temperature of the mixer may be achieved by circulating hot water having a temperature at which the organic solvent or water is evaporated, preferably about 50 to 100°C, around the mixer, the hot water may be cooled by circulating it around the mixer, and the cooled water may be heated by a heat exchanger, at which time and the heated water may then be re-circulated.

The mixer may be any mixer so long as the lithiated compound and the coating solution are well mixed and the temperature of the mixer is raised during the mixing process. Preferred is a mixer into which the blowing gas can be injected and which can keep a vacuum condition. Exemplary of the mixer may be a planetary mixer. FIG. 1 presents a mixer with a heat exchanger. As shown in FIG. 1, nitrogen gas (blowing gas) is injected into the upper portion of the mixer while the hot water is circulated through the heat exchanger around the mixer.

Thereafter, the coated powder may be dried from room temperature to about 200°C for approximately 1 to 24 hours.

If the one-shot process is performed, the drying step may be simultaneously performed with the coating step, thus eliminating the requirement of the additional drying step.

According to the drying step, the coating element-containing organic solution or coating element-containing aqueous solution is converted into hydroxide. As a result, a surface-treatment layer including metal hydroxide is formed on the surface of the positive active material. By varying the drying atmosphere, the surface-treatment layer may include oxyhydroxide, oxycarbonate, or hydroxycarbonate. For example, when the drying step is performed under a carbon dioxide atmosphere, oxycarbonate or hydroxycarbonate is formed. In addition, the surface-treatment layer may include at least two selected from metal hydroxide, metal oxyhydroxide, metal oxycarbonate and metal hydroxycarbonate.

The surface-treatment layer preferably has a thickness of about 1 to 100nm, more preferably 1 to 50nm. While other thicknesses are possible, if the thickness of the surface-treatment layer is less than 1nm, the effect obtained from the surface-treatment layer may not be realized, and in contrast, if the thickness is more than 100nm, the surface-treatment layer may become undesirably thick reducing specific energy of the active material.

The content of coating element in the surface-treatment layer is preferably about 2×10^{-5} to 1 percent by weight based on the weight of the positive active material, and more preferably 0.001 to 1 percent by weight.

The forming procedure of the surface-treatment layer including coating element-included hydroxide according to one embodiment of the present invention is schematically illustrated in FIG. 2. The surface-treatment layer reduces the internal resistance and prevents the discharge potential drop so that the active material exhibits high discharge potential, and as a result, the positive active material of the present invention provides good cycle life characteristics, discharge potential, and power, and it also exhibits superior charge and discharge characteristics as compared to that of metal oxide-coated positive active material.

This inventive procedure includes the mixing step and the drying step. The conventional procedure includes the mixing step, the drying step, and the heat-treating step (FIG. 3). As shown in FIGs. 2 and 3, whether the heat-treating step is performed or not, the type of material on the surface of lithiated compound is changed. When the heat-treating step is performed, a metal oxide layer is formed on the core. The metal oxide layer has relatively low

ionic conductivity, which causes the internal resistance to increase and the discharge potential and power density to deteriorate. On the other hand, when the heat-treating step is not performed, a surface-treatment layer including coating element-included hydroxide, oxyhydroxide, oxycarbonate, hydroxycarbonate or a mixture thereof is formed on the core. The surface-treatment layer reduces the internal resistance and prevents the discharge potential drop so that the active material exhibits high discharge potential. The positive active material of the present invention exhibits superior charge and discharge characteristics as compared to that of metal oxide-coated positive active material.

For reference purposes, the one-shot process is compared with the conventional process below, and their procedures are illustrated in FIG. 4. As shown in FIG. 4, the conventional coating process is such that the coating element-containing organic solution or aqueous solution is mixed with the lithiated compound to make a slurry (mixing step). The resulting lithiated compound is separated from the solution (solvent removing step), the separated lithiated compound is dried, perhaps at 80 to 100°C (drying step), and then the dried compound is heat-treated.

The inventive procedure, also shown in FIG. 4, includes a one-shot process (including the mixing step, the solvent removing step and the drying step in a single vessel) so that the total procedure is simple and economical, and furthermore, this procedure uniformly coats the lithiated compound with the coating element-containing organic solution or aqueous solution. The positive

active material preparation of the present invention includes no heat-treating step so that the total required time for preparing positive active material is reduced and the cost for the heat-treating step is eliminated.

In order to separate particles with desirable average diameter, the positive active material powder may or may not be sieved. Where there is no sieving, the same material that is included in the surface-treatment layer remains in the positive active material slurry. The material, metal hydroxide, metal oxyhydroxide, metal oxycarbonate, metal hydroxycarbonate, or a mixture thereof, in the slurry improves the thermal stability of the positive electrode.

In order to be marketable, batteries should pass various stability tests, and the penetration test in which a nail is passed through a charged battery, is critical for guaranteeing the stability of the battery. The stability of the battery depends on various factors, especially exothermic reaction caused by reacting the charged positive electrode with electrolyte immersed in the charged positive electrode.

For example, when a coin cell with a LiCoO_2 active material is charged to a pre-determined potential, LiCoO_2 is converted to $\text{Li}_{1-x}\text{CoO}_2$, and the differential scanning calorimetry (DSC) result of the charged active material, $\text{Li}_{1-x}\text{CoO}_2$, has been expected to provide thermal stability of the active material. Because the $\text{Li}_{1-x}\text{CoO}_2$ active material is unstable, oxygen, bonded with metal (Co-O), decomposes according to increases in temperature in order to release oxygen. The released oxygen may react with an electrolyte in a cell to cause the cell to explode. Accordingly, the temperature and the quantity of heat evolved when oxygen is decomposed significantly affect the stability of the cell.

The positive active material of the present invention has about 230°C or more of the exothermic temperature, which is 30°C higher than that of the positive active material without the surface-treatment layer, and furthermore, the positive active material of the present invention has a small quantity of heat evolved during the exothermic reaction so that the positive active material of the present invention exhibits superior thermal stability.

The lithiated compound may be available commercially or may be produced by the following procedure.

Lithium sources are mixed with metal sources in a desirable ratio. The lithium source may be any material known in the related art, some of which include lithium nitrate, lithium acetate, and lithium hydroxide. For the metal sources, manganese sources, cobalt salts, nickel sources, or nickel-manganese sources may be used. Typical examples of the manganese sources are manganese acetate and manganese dioxide. Typical examples of the cobalt sources are cobalt hydroxide, cobalt nitrate and cobalt carbonate, whereas typical examples of the nickel sources are nickel hydroxide, nickel nitrate, and nickel acetate. The nickel-manganese sources are produced by co-precipitating nickel and manganese salts. Fluoride sources, sulfur sources or phosphorous sources may be further used together with the manganese sources, cobalt sources, nickel sources or nickel-cobalt sources. The fluoride sources may be manganese fluoride or lithium fluoride and the sulfur sources may be manganese sulfide or lithium sulfide. The phosphorous sources may be H_3PO_4 . Note that the above list of manganese, cobalt, nickel, nickel-

manganese, fluoride, sulfur and phosphorus sources is not an exclusive list.

The mixing procedure may be performed by mortar grinder mixing, and at this time, in order to facilitate the reaction of the lithium sources and the metal sources, a solvent such as ethanol, methanol, water or acetone, is added to the mixture, and the mixture is then mortar grinder mixed until a liquid-free condition is reached.

The resulting mixture is heat-treated at about 400 to 600°C to produce a semi-crystalline positive active material precursor powder represented by formulas 1 to 9. Although other temperatures are possible, if the first heat-treating step temperature is less than 400°C, the metal sources may not react completely with the lithium sources. Thereafter, the heat-treated active material precursor powder is dried under dry air or oxygen, and the precursor powder is remixed to uniformly distribute the lithium sources. Alternatively, the remixing step may be performed immediately after the heat-treating step.

The semi-crystalline precursor powder is again heat-treated at about 700 to 900°C for about 10 to 15 hours to produce a crystalline positive active material. If the second heat-treating step temperature is less than 700°C, it may be difficult to form a crystalline material. The heating step may be performed by increasing the temperature at a rate of 1 to 5°C/min under dry air. The mixture is allowed to stand at the first and second heat-treating temperature for predetermined amounts of time, and then mixture is naturally

cooled.

As a result, a powder of a compound selected from the group consisting of the compounds represented by formulas 1 to 9 is obtained, and thereafter, the compounds represented by formulas 1 to 9 are shaken at room temperature to uniformly distribute the lithium sources.

The following examples further illustrate the present invention.

Comparative example 1

A LiCoO_2 with an average diameter of $10\text{ }\mu\text{m}$, positive active material, a conductive agent and a binder were mixed in N-methyl pyrrolidone at a weight ratio of 94 : 3 : 3 to make a positive active material slurry. As the conductive agent, Super P was used, and as the binder, polyvinylidene fluoride was used. The positive active material slurry is cast on an Al-foil with a thickness of about $100\text{ }\mu\text{m}$ to make a positive electrode. The positive electrode was punched at a diameter of 1.6cm, and a coin-type half-cell was fabricated in a glove-box using the punched positive electrode, a 1M LiPF_6 in ethylene carbonate and dimethyl carbonate electrolyte, and a lithium metal foil counter electrode.

Comparative example 2

A coin-type half-cell was fabricated by the same procedure as in Comparative example 1, except that LiMn_2O_4 with an average diameter of $15\text{ }\mu\text{m}$ was used.

Comparative example 3

A coin-cell was fabricated by the same procedure as in Comparative

example 1, except that $\text{LiNi}_{0.9}\text{Sr}_{0.002}\text{Co}_{0.1}\text{O}_2$ positive active material was used.

Comparative example 4

One percent by weight of Al-isopropoxide was dissolved in 99 percent by weight of ethanol to prepare a 1% Al-isopropoxide ethanol solution. To the ethanol solution, LiCoO_2 with an average diameter of 10 μm was added. Then they were well mixed to sufficiently react the ethanol solution with LiCoO_2 . The resulting material was separated from the solution and then dried at 100°C for about 12 hours in an oven. The dried material was heat-treated at about 500°C for approximately 10 hours under dry air. As a result, a positive active material with an Al_2O_3 surface layer was prepared.

The positive active material powder, a carbon conductive agent, and a polyvinylidene fluoride binder were mixed in a N-methyl pyrrolidone solvent at a ratio of 94 : 3 : 3 to make a positive active material slurry. The positive active material slurry was cast on an Al-foil with a thickness of about 100 μm to make a positive electrode. The positive electrode was punched at a diameter of 1.6cm, and a coin-type half-cell was fabricated in a glove-box using the punched positive electrode, a 1M LiPF_6 in ethylene carbonate and dimethyl carbonate electrolyte, and a lithium metal foil counter electrode.

Comparative example 5

A coin-type half-cell was fabricated by the same procedure in Comparative example 4, except that 5% Al-isopropoxide ethanol solution was used and the heat-treatment was performed at 600°C.

Comparative example 6

A coin-type half-cell was fabricated by the same procedure in Comparative example 4, except that $\text{LiNi}_{0.9}\text{Sr}_{0.002}\text{Co}_{0.1}\text{O}_2$ positive active material was used.

Comparative example 7

A coin-type half-cell was fabricated by the same procedure in Comparative example 4, except that 1% Al-isopropoxide ethanol solution and $\text{LiNi}_{0.9}\text{Sr}_{0.002}\text{Co}_{0.1}\text{O}_2$ positive active material were used.

Comparative example 8

A coin-type half-cell was fabricated by the same procedure in Comparative example 4, except that the heat-treatment was performed at 600°C.

Example 1

One percent by weight of Al-isopropoxide powder was dissolved in 99 percent by weight of ethanol to prepare a 1% Al-isopropoxide solution.

The Al-isopropoxide solution and LiCoO_2 with an average diameter of 10 μm were injected into a mixer shown in FIG. 1 and they were mixed for about 10 minutes. The temperature of an incubator was set to about 60°C, and the mixing step was performed for about 1 hour while the water was circulating and N_2 gas was purging. As a result, LiCoO_2 positive active material powder with $\text{Al}(\text{OH})_3$ surface layer was prepared.

The positive active material powder, a conductive agent, and a binder

were mixed in a N-methyl pyrrolidone solvent at a ratio of 94 : 3 : 3 to make a positive active material slurry. As the conductive agent, Super P was used, and as the binder, polyvinylidene fluoride was used. The positive active material slurry was cast on an Al-foil with a thickness of about 100 μm to make a positive electrode. The positive electrode was punched with a diameter of 1.6cm, and a coin-type half-cell was fabricated in a glove-box using the positive electrode, a 1M LiPF_6 in ethylene carbonate and dimethyl carbonate electrolyte, and a lithium metal counter electrode.

Example 2

One percent by weight of Al-isopropoxide was dissolved in 99 percent by weight of ethanol to prepare a 1% Al-isopropoxide ethanol solution. To the ethanol solution, LiCoO_2 with an average diameter of 10 μm was added. Then they were well mixed to sufficiently react the ethanol solution with LiCoO_2 . The resulting material was separated from the solution and then dried at about 100°C for about 12 hours in an oven to prepare a positive active material. Using the positive active material, a coin-type half-cell was fabricated by the same procedure in Example 1.

Example 3

A coin-type half-cell was fabricated by the same procedure in Example 2, except that a 5% Al-isopropoxide solution was used.

Example 4

A coin-type half-cell was fabricated by the same procedure in Example

2, except that 10% Al-isopropoxide solution was used.

Example 5

A coin-type half-cell was fabricated by the same procedure in Example 2, except that a $\text{Al}(\text{OH})_3$ coated LiCoO_2 positive active material was prepared by using a 10% Al-isopropoxide solution followed by passing it through a 325 mesh ($44\ \mu\text{m}$) screen to collect a powder with an average diameter of less than $44\ \mu\text{m}$.

Example 6

A coin-type half-cell was fabricated by the same procedure in Example 2, except that $\text{LiNi}_{0.9}\text{Sr}_{0.002}\text{Co}_{0.1}\text{O}_2$ was used instead of LiCoO_2 .

Example 7

A coin-type half-cell was fabricated by the same procedure in Example 2, except that $\text{LiNi}_{0.9}\text{Sr}_{0.002}\text{Co}_{0.1}\text{O}_2$ was coated with a 5% Al-isopropoxide solution.

Example 8

A coin-type half-cell was fabricated by the same procedure in Example 2, except that a 1% aluminum nitrate solution prepared by adding $\text{Al}(\text{NO}_3)_3$ in water was used and the drying step was performed in an oven at about 100°C for approximately 24 hours.

Example 9

A coin-type half-cell was fabricated by the same procedure in Example 2, except that a 5% aluminum nitrate solution prepared by adding $\text{Al}(\text{NO}_3)_3$ in

water was used and the drying step was performed in an oven at about 100°C for approximately 24 hours.

Example 10

A coin-type half-cell was fabricated by the same procedure in Example 2, except that a 10% aluminum nitrate solution prepared by adding $\text{Al}(\text{NO}_3)_3$ in water was used and the drying step was performed in an oven at about 100°C for approximately 24 hours.

Example 11

One percent by weight of B_2O_3 was dissolved in 95 percent by weight of ethanol to prepare a boron ethoxide solution. LiCoO_2 powder, with an average diameter of 10 μm , was dipped into the ethoxide solution, and then they were well mixed to sufficiently react a surface of LiCoO_2 powder with boron ethoxide followed by drying the resulting material dried in an oven at about 100°C for approximately 12 hours to prepare a LiCoO_2 positive active material powder with $\text{BH}(\text{OH})_2$ surface layer. Using the positive active material, a coin-type half-cell was fabricated by the same procedure in Example 2.

Example 12

A coin-type half-cell was fabricated by the same procedure in Example 11, except that a 5% boron ethoxide solution was used.

Example 13

A coin-type half-cell was fabricated by the same procedure in Example 11, except that a 10% boron ethoxide solution was used.

Example 14

A coin-cell was fabricated by the same procedure in Example 11, except that LiMn_2O_4 powder with an average diameter of $15\ \mu\text{m}$ and coated with a 1 % boron ethoxide solution was used.

Example 15

A coin-cell was fabricated by the same procedure in Example 11 except that LiMn_2O_4 powder with an average diameter of $15\ \mu\text{m}$ and coated with a 10 % boron ethoxide solution was used.

Example 16

A coin-cell was fabricated by the same procedure in Example 11 except that $\text{Li}_{1.03}\text{Ni}_{0.69}\text{Mn}_{0.19}\text{Co}_{0.1}\text{Al}_{0.07}\text{Mg}_{0.07}\text{O}_2$ coated with a 1 % boron ethoxide solution was used.

Example 17

A coin-cell was fabricated by the same procedure in Example 11 except that $\text{LiNi}_{0.9}\text{Co}_{0.1}\text{Sr}_{0.002}\text{O}_2$ coated with a 1 % boron ethoxide solution was used.

SEM photographs of the positive active materials

The SEM photographs of the positive active materials according to Examples 2 and 3, and Comparative example 5 are presented in FIGs. 5a, 5b and 5c, respectively. For comparison, SEM photograph of pure LiCoO_2 is presented in FIG. 5d. As shown in FIGs. 5a-d, the positive active materials according to Examples 2 and 3 (FIGs. 5a and 5b) have similar smooth surface to that of LiCoO_2 (FIG. 5d), but the positive active material according to Comparative example 5 (FIG. 5c) has an uneven surface due to the metal

oxide mass.

TEM photographs of the positive active materials

The TEM photographs of the positive active materials according to Example 2 and Comparative example 5 are presented in FIGs. 6a and 6b, respectively. FIG. 6a indicates that the positive active material according to Example 2 has an amorphous $\text{Al}(\text{OH})_3$ surface layer. Whereas FIG. 6b indicates that the positive active material according to Comparative example 5 has a Co-Al-O (CoAl_2O_4) surface layer and Al_2O_3 mass on the layer.

XRD pattern of the positive active materials

The XRD results of the positive active materials according to Examples 2 to 5 and Comparative example 1 are presented in FIG. 7. It was shown from FIG. 7 that the XRD patterns of the positive active materials according to Examples 2 to 5 are similar to those according to Comparative example 1. These results indicate that the surface-treatment layer may be formed without modification of the bulk chemical structure of the positive active materials.

Charge and discharge characteristics

The positive active materials according to Examples 2 to 5, and Comparative examples 1 and 8, were charged and discharged at 0.1C and 1C, respectively, and the discharge characteristics thereof are shown in FIGs. 8 and 9, respectively. The positive active materials according to Examples 2 to 5 exhibited slightly better discharge characteristics than those of Comparative example 8 at a low rate (FIG. 8, 0.1C), but at high rate (1C) Examples 2 to 5 exhibited surprisingly better discharge characteristics than that of Comparative example (FIG. 9).

Cycle life characteristics

The cycle life characteristics of the positive active materials according to Examples 2 to 5 and Comparative example 1 were measured. While the charge and discharge rates (current density) were varied in order of 0.1C (1 cycle), 0.2C (3 cycles), 0.5C (10 cycles) and 1C (10 cycles), the positive active materials were charged and discharged between 4.3V to 2.75V, and the results are shown in FIG. 10. For easy comparison, the discharge capacity of first cycle at each rate was measured and the results are shown in Table 1.

Table 1: Discharge capacity according to C-rate [unit: mAh/g]

C-rate	0.1C	0.5C	1C
Comparative example 1	159	150	137
Example 2	162	157	152
Example 3	159	154	152
Example 4	164	159	149
Example 5	159	153	145

As shown in Table 1, the positive active materials according to Examples 2 to 5 exhibited better cycle life characteristics than Comparative example 1 (LiCoO₂ without surface-treatment).

The cycle life characteristics of the positive active materials according to Examples 14 to 15 and Comparative example 2 (LiMn₂O₄ without surface-treatment) were measured by increasing C rates between 4.3V to 2.75V at a high temperature, 60°C, and the results are shown in FIG. 11. It was shown from FIG. 11 that the initial discharge capacities of the cells according to

Examples 14 to 15 were superior to that according to Comparative example 2. The cell according to Comparative example 2 exhibited abrupt discharge capacity loss after 30 cycles, and on the other hand, the discharge capacities of the cells according to Examples 14 to 15 remained almost the same after 30 cycles. These good cycle life characteristics at high temperatures are achieved from HB(OH)_2 on the surface of LiMn_2O_4 , which protects the dissociation of Mn from LiMn_2O_4 , which results in the deterioration of the cycle life characteristics. As a result, it is expected that the positive active materials according to Examples 14 to 15 had pronouncedly reduced deterioration of the cycle life characteristics associated with the dissolution of Mn from LiMn_2O_4 .

Average discharge potential

The coin-cells with the positive active materials according to Examples 2 to 5, and Comparative examples 1 and 8 were charged and discharged between 4.3V to 2.75V by varying the rates, i.e., 0.1C (1 cycle), 0.2C (3 cycles), 0.5C (10 cycles) and 1C (10 cycles), and the average discharge potential was measured and the results are presented in Table 2.

Table 2 : Average discharge potential according to C-rate (unit: volt)

C-rate	0.1C	0.5C	1C
Comparative example 1	3.92	3.89	3.81
Comparative example 8	3.92	3.90	3.86
Example 2	3.92	3.91	3.89
Example 3	3.92	3.91	3.88
Example 4	3.92	3.91	3.88
Example 5	3.92	3.91	3.87

As shown in Table 2, the average discharge potential of the coin cells according to Examples 2 to 5 were similar to that of Comparative example 1 at a low rate (0.1C), but they were significantly higher than that of Comparative example 1 at a high rate (1C) by 0.06V or more. Furthermore, the coin cells with the positive active material of Examples 2 to 5 had higher average discharge potential than that of Comparative example 8 with a heat-treatment step. That is, the coin cells with the positive active material of the present invention has higher discharge potential.

The positive active material according to Comparative example 8 had a surface layer including metal oxide with relatively low ionic conductivity which causes increase in the internal resistance and reduced discharge potential and power, and on the other hand, the metal hydroxide-included surface-treatment layer in the positive active materials according to Examples 2 to 5 had relatively low internal resistance so that it exhibits low discharge potential drop and high discharge potential retention. Thus, it is expected that the cell with the positive

active material of Example 2 to 5 exhibited good cycle life characteristics, discharge potential characteristics and improved power density.

Thermal stability

In order to identify the thermal stability of the positive active materials of the present invention, the DSC analysis were performed the following procedure. After the coin cells according to Examples 4 and 5, and Comparative examples 1 and 8 were charged to 4.3V, and the charge capacities thereof were measured and the results are shown in Table 3.

Table 3

	Comparative example 1	Comparative example 8	Example 4	Example 5
Charge capacity [mAh/g]	165	163	168	162
OCV after charging [V]	4.28	4.28	4.28	4.28

All positive active materials had charge capacities of 162 to 168mAh/g and OCV of 4.28V.

The positive electrode was separated from the coin cell charged to 4.3V in a dry room. About 10 mg of the positive active material was collected from the electrode and DSC analysis was performed with a 910 DSC (TA instruments). DSC analysis was performed by scanning from 25 to 300°C with temperature increasing at a rate of 3 °C/min. The DSC analysis results are

presented in FIG. 12.

As shown in FIG. 12, LiCoO_2 according to Comparative example 1 exhibited a large exothermic peak in the range of about 190 to 220°C. After charging a lithium cell, a structure of a positive active material is converted from LiCoO_2 to $\text{Li}_{1-x}\text{CoO}_2$, the Co-O bond in $\text{Li}_{1-x}\text{CoO}_2$ is too weak to decompose and to release O_2 and the release of oxygen may react with an electrolyte in a cell to cause the cell to explode. The exothermic peak occurs by reacting the released O_2 with an electrolyte. The positive active material of Comparative example 8 had a smaller exothermic peak than that of Comparative example 1, but decomposition temperature thereof is shifted to the right (higher temperature). The positive active materials according to Examples 4 and 5 had an exothermic peak in the range of 240 to 250°C shifted from about 190 to 220°C. As a result, the positive active materials according to Examples 4 and 5 had exothermic peaks that occurred about 30°C higher than that according to Comparative examples 1 and 8. In addition, the peak areas of Examples 4 and 5 are dramatically smaller than that of Comparative example 1. Thus, the amount of heat evolved in Examples 4 and 5 is smaller than that of Comparative examples. The increase in the decomposition temperature (the oxygen released temperature) and the reduced amount of heat indicate that the positive active materials according to Examples exhibited better thermal stability than that according to Comparative examples. Especially, the positive active material of Example 4 produced without sieving exhibits better thermal stability

than that of Example 5 produced with sieving. It is believed that the aluminum oxyhydroxide ($\text{AlO}(\text{OH})$) or aluminum hydroxide ($\text{Al}(\text{OH})_3$) that remained in the positive active material of Example 4 helps to improve thermal stability.

The DSC analysis of the positive active material of Example 13 was performed by the same procedure as in Examples 4 and 5 and the result is shown in FIG. 13. For comparison, that of Comparative example 1 is also shown in FIG. 13. In this FIG. 13, the positive active material of Example 13 had a decomposition temperature of 30°C higher than that of Comparative example 1 and had smaller heat evolved than that of Comparative example 1.

Twenty cylindrical cells with 2000 mAh using the positive active materials according to Examples 4 to 5, and Comparative examples 1 and 8 were fabricated, respectively. The pictures of the cells of Comparative example 8 and Example 4 prior to and after the heat with a burner are shown in FIG. 14a to 14b, respectively. The cells of Comparative examples 1 and 8 were mostly exploded, but that of Examples 4 and 5 were not exploded. The firing test results are presented with an explosion rate obtained from the rates of numbers of exploded cells to total cells, the exposure to heat test results are obtained at the time at which the cells are exploded, which occurs when the cells are exposed to a temperature of about 150°C, and the overcharge test results are obtained from leak percentages when the cells are overcharged at 1C rate. These results are presented in Table 4.

Table 4

	Comparative	Comparative	Example 4	Example 5
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	example 1	example 8		
Explosion percentage	100%	70%	0%	0%
Time (average)	10 min.	12 min.	18 min.	20 min.
Leak percentage	100%	60%	0%	0%

Structure of the surface-treatment layer

In order to identify amorphous $\text{Al}(\text{OH})_3$ and Al_2O_3 , the XRD pattern thereof were measured. The amorphous $\text{Al}(\text{OH})_3$ and Al_2O_3 were prepared by mixing 5g of a Al-isopropoxide solution and 95g of ethanol, mixing them for about 3 hours to obtain clear Al-isopropoxide solution, and dividing the solution into three beakers. Thereafter, the No. 1 beaker was dried at about room temperature for about 1 day (Sample 1), the No. 2 beaker was dried in an approximately 130°C oven for about 1 day (Sample 2) and the No. 3 beaker was heat-treated in an approximately 600°C furnace for about 1 day (Sample 3).

The structure of the surface of the sample 1 powder was identified by a FT-IR analysis of a pellet mixed with the sample 1 powder and KBr, and the result is shown in FIG. 15 and labeled as (a). The FT-IR result of the sample 1 powder with an ATR (Attenuated Total Reflectance) method is shown in FIG. 15 and labeled as (b). By this FT-IR result, it was deduced that the structure of the surface is $\text{AlO}(\text{OH})$.

The Raman spectrum analysis of the sample 1 powder and Al_2O_3 were performed and the results are presented in FIG. 16. As shown in FIG. 16, the sample 2 powder had a different pattern from Al_2O_3 .

The XRD patterns of the powder dried at about 130°C (Sample 2: amorphous $\text{Al}(\text{OH})_3$) and the powder heat-treated at about 600°C (Sample 3: Al_2O_3) are shown in FIG. 17. It is evident from FIG. 17 that the XRD pattern of amorphous $\text{Al}(\text{OH})_3$ is distinct from that of amorphous Al_2O_3 . Both powder had amorphous patterns. It is considered that the powder dried at 130°C is $\text{Al}(\text{OH})_3$ presented in JCPDS No. 83-2256 and that heat-treated at 600°C is amorphous Al_2O_3 presented in JCPDS No. 02-1373, when they are compared with the reference datum in JCPDS cards of FIG. 18. Accordingly, it is expected that the positive active materials according to Examples 1 to 10 have amorphous coating layer.

A mixture of 5g of B_2O_3 with 95g of ethanol was shaken for about 1 hour to prepare a clear and transparent 5% $\text{BH}(\text{OH})_2$ solution. The solution was dried in an oven at about 100°C for approximately 10 hours to obtain white miniscule powder (Sample 4). The XRD pattern of sample 4 and the commercial B_2O_3 are presented in FIG. 19. It is evident from FIG. 19 that the commercial B_2O_3 has no clear single phase, but the sample 4 has a clear single phase. The XRD pattern of sample 4 corresponded to JCPDS card No. 82-1067, and thus, it is crystalline hydrogen borate ($\text{HB}(\text{OH})_2$). These results

indicated that the surface of the positive active materials according to Examples 11 to 15 had a crystalline form.

[Effect of the invention]

In summary, the positive active material of the present invention has metal hydroxide layer having good ionic conductivity, which reduces internal resistance and prevents the discharge potential drop. The positive active material of the present invention provides rechargeable lithium battery exhibiting good cycle life characteristics, high discharge potential and high power.

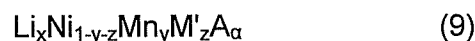
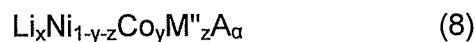
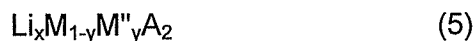
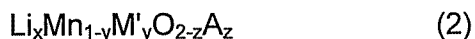
[WHAT IS CLAIMED IS:]

1. A positive active material for a rechargeable lithium battery comprising

a core comprising at least one lithiated compound; and

a surface-treatment layer on the core comprising at least one coating material selected from the group consisting of coating element included-hydroxides, oxyhydroxides, oxycarbonates, hydroxycarbonates and a mixture thereof.

2. The positive active material of claim 1 wherein the lithiated compound is at least one lithiated compound represented by the formulas 1 to 9,



where

$$0.95 \leq x \leq 1.1, 0 \leq y \leq 0.5, 0 \leq z \leq 0.5, 0 \leq \alpha \leq 2,$$

M is Ni or Co, M' is at least one element selected from the group consisting of Al, Ni, Co, Cr, Fe, Mg, Sr, V, Sc, Y, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Ac, Th, Pa, U, Np, Pu, Am, Cm, Bk, Cf, Es, Fm, Md, No and Lr, M'' is at least one element selected from the group consisting of Al, Cr, Mn, Fe, Mg, Sr, V, Sc, Y, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Ac, Th, Pa, U, Np, Pu, Am, Cm, Bk, Cf, Es, Fm, Md, No and Lr, and A is selected from the group consisting of O, F, S and P.

3. The positive active material of claim 1 wherein the coating element of the coating material is soluble in organic solvents or water.

4. The positive active material of claim 3 wherein the coating element of the coating material is at least one element selected from the group consisting of Mg, Al, Co, K, Na, Ca, Si, Ti, Sn, V, Ge, Ga, B, As, Zr, and a mixture thereof.

5. The positive active material of claim 1 wherein the coating material has amorphous or crystalline form.

6. The positive active material of claim 1 wherein the surface-treatment layer has a thickness in the range of 1 to 100nm.

7. The positive active material of claim 6 wherein the surface-treatment layer has a thickness in the range of 1 to 50nm.

8. The positive active material of claim 1 wherein the content of the coating element of the coating material is 2×10^{-5} to 2 percent by weight based on the weight of the positive active material.

9. The positive active material of claim 8 wherein the content of the coating element of the coating material is 0.001 to 1 percent by weight

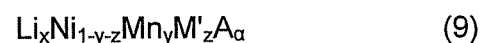
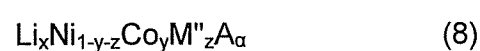
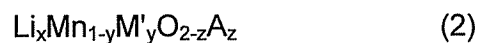
based on the weight of the positive active material.

10. A method of preparing a positive active material for a rechargeable lithium battery comprising:

coating at least one lithiated compound with an organic solution of coating material source or an aqueous solution of coating material source to produce a coated compound; and

drying the coated compound.

11. The method of claim 10 wherein the lithiated compound is at least one lithiated compound represented by formulas 1 to 9,



where

$$0.95 \leq x \leq 1.1, 0 \leq y \leq 0.5, 0 \leq z \leq 0.5, 0 \leq \alpha \leq 2,$$

M is Ni or Co, M' is at least one element selected from the group consisting of Al, Ni, Co, Cr, Fe, Mg, Sr, V, Sc, Y, La, Ce, Pr, Nd, Pm, Sm,

Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Ac, Th, Pa, U, Np, Pu, Am, Cm, Bk, Cf, Es, Fm, Md, No and Lr, M" is at least one element selected from the group consisting of Al, Cr, Mn, Fe, Mg, Sr, V, Sc, Y, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Ac, Th, Pa, U, Np, Pu, Am, Cm, Bk, Cf, Es, Fm, Md, No and Lr, and A is selected from the group consisting of O, F, S and P.

12. The method of claim 10 wherein the organic solution of coating material source is prepared by adding a coating material source to an organic solvent to form a mixture, the coating material source being selected from the group consisting of a coating element, a coating element included-alkoxide, salt and oxide.

13. The method of claim 10 wherein the mixture is refluxed to form the organic solution of coating material source.

14. The method of claim 10 wherein the aqueous solution of coating material source is prepared by adding a coating material source to water to form a mixture, the coating material source being selected from the group consisting of a coating element included-salt and oxide.

15. The method of claim 10 wherein the mixture is refluxed to form the aqueous solution of coating material source.

16. The method of claim 10 wherein the coating element of the coating material is soluble in organic solvents or water.

17. The method of claim 16 wherein the coating element of the coating material source is at least one element selected from the group consisting of Mg, Al, Co, K, Na, Ca, Si, Ti, Sn, V, Ge, Ga, B, As, Zr, and a mixture thereof.

18. The method of claim 10 wherein the concentration of coating material source in the organic solution or aqueous solution is 0.1 to 50 percent by weight.

19. The method of claim 18 wherein the concentration of coating material source in the organic solution or aqueous solution is 5 to 30 percent by weight.

20. The method of claim 10 wherein the coating step is performed by injecting the lithiated compound and the organic solution or the aqueous solution of coating material source into a mixer and continuously increasing the temperature within the mixer.

21. The method of claim 20 wherein the coating step further comprises injecting blowing gas into the mixer, or the coating step is performed under a vacuum.

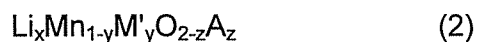
22. The method of claim 10 further comprising sieving the dried coated compound.

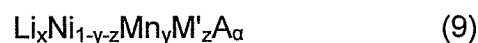
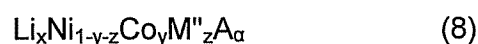
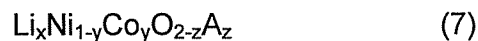
23. A positive active material for a rechargeable lithium battery comprising

a core comprising at least one lithiated compound; and

a surface-treatment layer on the core comprising coating element-included-hydroxide or oxyhydroxide.

24. The positive active material of claim 23 wherein the lithiated compound is at least one lithiated compound represented by formulas 1 to 9,





where

$$0.95 \leq x \leq 1.1, 0 \leq y \leq 0.5, 0 \leq z \leq 0.5, 0 \leq \alpha \leq 2,$$

M is Ni or Co, M' is at least one element selected from the group consisting of Al, Ni, Co, Cr, Fe, Mg, Sr, V, Sc, Y, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Ac, Th, Pa, U, Np, Pu, Am, Cm, Bk, Cf, Es, Fm, Md, No and Lr, M'' is at least one element selected from the group consisting of Al, Cr, Mn, Fe, Mg, Sr, V, Sc, Y, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Ac, Th, Pa, U, Np, Pu, Am, Cm, Bk, Cf, Es, Fm, Md, No and Lr, and A is selected from the group consisting of O, F, S and P.

25. The positive active material of claim 23 wherein the coating element of the surface treatment layer is soluble in organic solvents or water.

26. The positive active material of claim 25 wherein the coating element of the surface treatment layer is at least one element selected from the group consisting of Mg, Al, Co, K, Na, Ca, Si, Ti, Sn, V, Ge, Ga, B, As, Zr, and a mixture thereof.

27. The positive active material of claim 23 wherein the coating material has amorphous or crystalline form.

28. The positive active material of claim 23 wherein the content of the coating element of the surface-treatment layer is 2×10^{-5} to 1 percent by weight based on the weight of the positive active material.

29. The positive active material of claim 28 wherein the content of the coating element of the surface-treatment layer is 0.001 to 1 percent by weight based on the weight of the positive active material.

30. A positive active material for a rechargeable lithium battery comprising:

a core comprising a lithium-cobalt chalcogenide compound; and

a surface-treatment layer on the core comprising $\text{Al}(\text{OH})_3$ or, $\text{AlO}(\text{OH})$.

31. The positive active material of claim 30 wherein the content of Al of the surface-treatment layer is 2×10^{-5} to 1 percent by weight based on the weight of the positive active material.

32. The positive active material of claim 30 wherein the content of Al of the surface-treatment layer is 0.001 to 1 percent by weight based on the weight of the positive active material.

33. A positive active material for a rechargeable lithium battery comprising:

a core comprising a lithium-manganese chalcogenide compound; and

a surface-treatment layer on the core comprising $\text{HB}(\text{OH})_2$.

34. The positive active material of claim 33 wherein the content of B of the surface-treatment layer is 2×10^{-5} to 1 percent by weight based on the

weight of the positive active material.

35. The positive active material of claim 34 wherein the content of B of the surface-treatment layer is 0.001 to 1 percent by weight based on the weight of the positive active material.